Abstract No. Ran0379

A Synchrotron WAXD Study on the Early Stages of Coagulation during PBO Fiber Spinning

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Beamline(s): X27C

Introduction: Poly(*p*-phenylene benzobisoxazole) (PBO) fibers are known to possess the highest tensile modulus and strength among all commercial synthetic polymer fibers. [1-2] The general manufacturing method for PBO fibers starts with a dry-jet wet-spinning process from the polymer solution in poly(phosphoric acid) (PPA). After spinning, the fiber is coagulated in water to remove the solvent (PPA). The coagulation process is a critical step in the PBO fiber structure formation. In a previous work, we have studied the structural changes of the PBO fiber during the spinning process by *in situ* synchrotron wide-angle X-ray diffraction (WAXD). [2] Our results showed that a significant molecular ordering took place after the fiber had passed through the coagulation water bath at temperatures ranging from 25-60 °C. Although the coagulation process was found to strongly affect the final PBO fiber structure, the evolution of the structural changes in the coagulation process has not been sufficiently investigated. In the present study, a unique modification was made to the spinning apparatus, which allowed us to probe the coagulating fiber after coagulation with a time period as short as 0.03 sec. This modified spinning apparatus was used to examine the effects of the coagulation time on the structural development in the PBO fiber using the *in situ* synchrotron WAXD technique.

Methods and Materials: The spinning experiment was carried out at the Advanced Polymers Beamline X27C of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The X-ray wavelength was 0.137 nm. The spinning unit was a modified version of the experimental unit constructed by the DOW Chemical Company, which has been described in detail elsewhere. [2] The exit orifice of the spinneret had a diameter of 0.3 mm and a length of 0.3 mm. A new water bath was designed to meet the requirements of short coagulation times. The accessible range of coagulation times was 0.03-0.3 sec. The PBO/PPA dope was inserted into the preheated barrel having an inner diameter of 9.52 mm. The dope was kept in the barrel at 160 ºC for about 50 min to reach the thermal equilibrium and was then extruded by a plunger. In the present study, the extrusion speed from the spinneret was fixed at about 64 mm/s. Two-dimensional WAXD images were recorded using a CCD X-ray detector (MAR-USA) after accumulation for about 2 min. The sample to detector distance was 118.9 mm. The collected WAXD images were corrected for beam intensity fluctuations and sample absorption.

Results: Fig.1 shows the one-dimensional equatorial scattered intensity of PBO filament with a spin-draw-ratio (SDR) of ~2.0 before coagulation and at different coagulation times. There were two scattering peaks on the equator before coagulation (Fig.1A) (at q = 0.65 $Å^{-1}$ and 1.41 $Å^{-1}$, corresponding to d-spacings of 9.67 Å and 4.45 Å, respectively). These two peaks could be related to the extruded PBO/PPA dope structure, possessing lyotropic liquid-crystalline characteristics with short-range order only in the cross section. After the fiber passed through the water bath, even if the coagulation time was as short as 0.03 sec (Fig.1B), an additional peak at q = 1.87 $Å^{-1}$ (d = 3.36 Å) appeared, which corresponded to the eventual 010 reflection of the final PBO crystal structure, implying that PPA-free stacks of flat PBO molecules had been formed immediately at the beginning of the coagulation process, probably forming a skin-core morphology with the coagulation starting near the fiber surface. With increasing coagulation time, this peak became stronger, indicating that more PPA-free PBO regions had been formed as more PPA molecules were hydrolyzed and washed away during coagulation. The eventual PBO 010 reflection was found to be formed ahead of the 200 reflection, which confirmed the concept that the first step of the coagulation was the formation of pure PBO stacks, with interstack order being formed later. The fraction of PPA-free PBO was found to reach almost 30% after 0.24 seconds of coagulation.

Conclusions: A water bath optimized for fast coagulation studies was designed and constructed to evaluate the structural development at the early stages of the coagulation process during PBO fiber spinning by using synchrotron wide angle X-ray diffraction. The results showed that PBO started to segregate into PPA-free PBO domains immediately when the fiber reached the water bath, even when the coagulation time was as short as 0.03 sec. The eventual PBO 010 reflection was found to be formed ahead of the 200 reflection, which confirmed the concept that the first step of the coagulation was the formation of pure PBO stacks, with interstack order being formed later.

Acknowledgments: The financial support of this work was provided by grants from the U.S. Army Research Office (DAAG559710022, DAAD190010419 and AASERT-DAAH049510307), the National Science Foundation (DMR9984102) and the US Department of Energy (DEFG 0286 ER45237.016). The loan of the solution spinning apparatus from the Dow Chemical Company is greatly appreciated.

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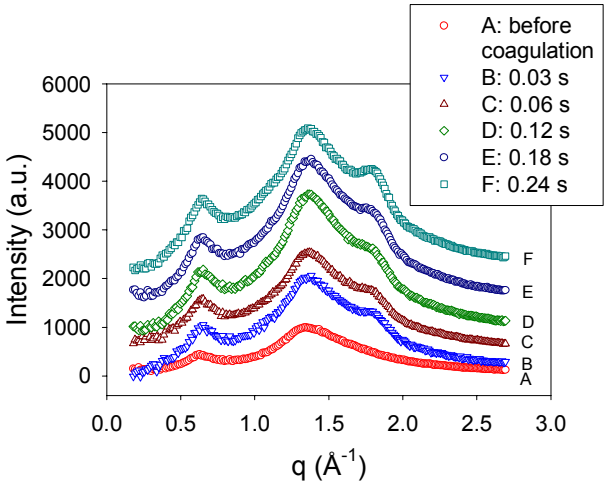

Figure 1. One-dimensional equatorial scattered intensity, obtained by averaging ±5º sectors on the equator of 2D scattering patterns, of PBO filament with a spin-draw-ratio (SDR) of ~2.0 before coagulation and at different coagulation times.